

PATENT ABSTRACTS OF JAPAN

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(21)Application number : 10-099613 (71)Applicant : ASAHI GLASS CO LTD

(22)Date of filing : 10.04.1998 (72)Inventor : SHIBUYA TAKASHI
HIRATSUKA KAZUYA

(54) ELECTRIC DOUBLE LAYER CAPACITOR AND ITS MANUFACTURE

(57)Abstract:

PROBLEM TO BE SOLVED: To extremely reduce the moisture in electrodes to hardly cause the performance deterioration by constituting an adhesive layer by curing a conductive adhesive contg. a conductive powder, epoxy resin, curing agent and solvent of a specified b. p. or less.

SOLUTION: Ethanol is added to and kneaded with a mixture of coconut husk active C powder, polytetrafluoroethylene and C black, the mixture is sheeted and roll-rolled to form an electrode sheet, an electrode sheet of about 40 mm square is cut from this sheet, adhered and fixed through a conductive adhesive to the surface of a etched Al foil collector and heated at a reduced pressure, 150°C or above to do the dry treatment. The conductive adhesive is prepared by mixing a conductive C black powder, bisphenol A type epoxy resin, curing agent of diethylene triamine and solvent of e.g. methyl ethyl ketone of a b. p. of 160°C or less.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to an electric double layer capacitor, especially the electric double layer capacitor excellent in actuation dependability.

[0002]

[Description of the Prior Art] In order that the electric double layer capacitor may make it the principle to accumulate a charge in the electric double layer formed in the interface of an electrode and the electrolytic solution and may raise the capacity consistency of an electric double layer capacitor, the particle of carbon materials, such as activated carbon of high specific surface area and carbon black, a metal, or conductive metallic oxide etc. is used for an electrode. In order to perform charge and discharge efficiently, the electrode is joined to small layers and foils of resistance of electronic conduction nature which are called a charge collector, such as a metal and a graphite. Stainless steel, such as bulb metals, such as corrosion resistance high ARUMIUMU, SUS304, and SUS316L, etc. is usually used for the electrochemistry target by the charge collector.

[0003] Although there are what used the organic electrolytic solution as the electrolytic solution, and a thing using the drainage system electrolytic solution in an electric double layer capacitor, operating potential is high and the electric double layer capacitor using the organic electrolytic solution attracts attention at the point which can enlarge the energy density of a charge condition. In order for moisture to electrolyze and to cause degradation of the engine performance if moisture exists in the interior of an electric double layer capacitor when using the organic electrolytic solution, it is necessary to fully dehydrate an electrode and desiccation processing heated under reduced pressure is usually performed.

[0004] Although activated carbon is mainly used for an electrode, since activated carbon is usually powdered, it mixes with the binder containing fluorine-containing resin, such as polytetrafluoroethylene (henceforth PTFE), and fabricates to a sheet-like electrode, and using as an electrode object electrically connected to the charge collector is known. At this time, there are also many things joined through the conductive glue line so that an electrode and a charge collector may be stuck and electric contact resistance may become small. However, it is difficult for fluorine-containing resin for adhesion to have the difficult property and to make bonding strength high.

[0005] Since electrochemical corrosion resistance is needed for a conductive glue line, it is desirable that nonmetal system ingredients, such as carbon black and a graphite, are contained as a filler which gives electronic conduction nature. In order to secure bonding strength furthermore, various binder components are used for a conductive glue line. As a binder component used for this purpose, inorganic system binder components (JP,2-82608,A), such as resin (JP,59-3915,A, JP,62-200715,A), such as a cellulose and polyvinyl alcohol, and water glass, and polyimide system resin (JP,9-270370,A) are known.

[0006] However, since the resistance over the organic electrolytic solution is inadequate when the electroconductive glue containing resin system binder components, such as a cellulose and polyvinyl alcohol, is used, an electrode and a charge collector are a lifting and a cone about exfoliation. Moreover,

since thermal resistance is around 120 degrees C, desiccation processing in an elevated temperature cannot be performed, but it is fully hard to remove the residual moisture which is sticking to activated carbon, and the residual moisture electrolyzes and there is a problem of the engine performance of an electric double layer capacitor deteriorating.

[0007] Moreover, with inorganic system binders, such as water glass, although thermal resistance is high, its bond strength of an electrode and a metal charge collector is inadequate, and it has the problem in which the performance degradation of an electric double layer capacitor occurs with the elution and the residual moisture of an alkali component. Although thermal resistance and an adhesive field are enough as polyimide system resin, in order to have to use the solvent of a polar high high-boiling point like a N-methyl-2-pyrrolidone as a solvent which dissolves resin, there is a problem in respect of removal of a solvent.

[0008]

[Problem(s) to be Solved by the Invention] This invention solves the trouble in the above-mentioned conventional technique, and there is very little moisture in an electrode, the bonding strength of an electrode and a charge collector is strong, removal of the solvent in adhesives is easy, and it aims at offering the electric double layer capacitor with which performance degradation cannot break out easily, and its manufacture approach.

[0009]

[Means for Solving the Problem] This invention offers the electric double layer capacitor characterized by said glue line coming to harden the electroconductive glue with which conductive powder, epoxy system resin, a curing agent, and the boiling point contain a solvent 160 degrees C or less in the electric double layer capacitor which has the organic electrolytic solution which forms an electric double layer in the interface of the electrode object which comes to join the electrode which makes a carbon material a subject to a charge collector through a glue line, and said electrode object.

[0010] In the electric double layer capacitor of this invention, although the binder component contained in electroconductive glue is an epoxy resin which consists of epoxy system resin, a curing agent, and a solvent of a low-boiling point, the glue line which comes to harden these adhesives is hardening resin which is excellent in the balance of thermal resistance and a mechanical strength, and was excellent in the adhesive strength of an electrode and a charge collector, corrosion resistance, etc.

[0011] As epoxy system resin used by this invention, since it excels in maintaining property balance, such as adhesive strength and thermal resistance, although various kinds of epoxy system resin can be used, and purity and workability, phenol system glycidyl ether molds, such as the bisphenol A type and a bisphenol F type, 1, 6-dihydroxy naphthalene mold, a phenol novolak mold, and a cresol novolak mold are suitable.

[0012] As such resin, for example Trade name:Epicoat 827 (oil-ized shell epoxy company make), Trade name : The bisphenol A type epoxy resins, such as D.E.R.331J (Dow Chemical Japan make), Trade name : Bisphenol F type epoxy resins, such as Epicoat 807 (oil-ized shell epoxy company make), Trade name: 1, such as HP-4032D (Dainippon Ink & Chemicals, Inc. make), 6-dihydroxy naphthalene type epoxy resin, Trade name: Phenol novolak type epoxy resins, such as Epicoat 154 (oil-ized shell epoxy company make), trade name: Cresol novolak type epoxy resins, such as Epicoat 180H65 (oil-ized shell epoxy company make), etc. are mentioned. These epoxy system resin may be used independently, or may mix and use two or more sorts.

[0013] Although each thing usually known as an epoxy system resin curing agent can use it as a curing agent used by this invention, the amine system curing agent which contains two or more amino groups of the 1st class or the 2nd class, such as diethylenetriamine, triethylenetetramine, and a meta-phenylenediamine, so that a hardened material may have thermal resistance, or especially a potential mold-curing agent like a dicyandiamide is desirable. These curing agents may be used independently, and two or more sorts may use them, mixing. Although the desirable addition of a curing agent changes greatly with the classes, it can be suitably chosen according to the setting time chosen in accordance with a production process.

[0014] As a solvent 160 degrees C or less, since the boiling point used by this invention can dissolve

epoxy system resin by high concentration, without solvents', such as n-butyl's cellosolve, not reacting with a methyl ethyl ketone as n-hexane and ketones, but reacting with epoxy system resin as Cellosolve Solvent as toluene, O-xylene, meta xylene, and an aliphatic series system solvent as an aromatic solvent, it is desirable. These solvents may be used independently, or may be used as two or more sorts of partially aromatic solvents, and they are added so that epoxy system resin may be dissolved and electroconductive glue may serve as desired viscosity.

[0015] Moreover, as for the rate of the total amount of the epoxy system resin and the curing agent which are contained in a conductive glue line, it is desirable that it is 10 - 70 % of the weight to the total amount of conductive powder, epoxy system resin, and a curing agent. At less than 10 % of the weight, if a good adhesive property is not acquired but it, on the other hand, exceeds 70 % of the weight, conductivity will fall rapidly.

[0016] In this invention, finishing agents, such as a curing catalyst and a coupling agent, and other additives may be blended into the adhesives for forming a conductive glue line if needed in addition to conductive powder, epoxy system resin, a curing agent, and the solvent of 160 degrees C or less of boiling points.

[0017] As a curing catalyst, in order to advance hardening promptly, little addition of the imidazole derivatives, such as 2-ethyl-4-methylimidazole and 1-benzyl-2-phenylimidazole, may be carried out, for example. Moreover, in order to improve wettability with the resin of conductive powder, and the dispersibility to the inside of resin, after blending finishing agents, such as about 1% of the weight of a fatty acid, and various silane coupling agents, to this powder and carrying out surface treatment of the conductive powder, you may use it. Moreover, in addition to this, a leveling agent, a dispersant, etc. may be added.

[0018] In this invention, electrochemical corrosion resistance is needed as conductive powder contained in a conductive glue line, and a nonmetal is desirable. Use of conductive carbon materials, such as carbon black and a graphite, is especially desirable.

[0019] In the electric double layer capacitor of this invention, since the epoxy resin after solvent removal which consists of the epoxy system resin and the curing agent which are the binder component of a conductive glue line has high thermal resistance, also after joining an electrode to a charge collector, it can fully carry out desiccation removal of the moisture in a carbon material by heat-treating under heating or reduced pressure under an elevated temperature. Moreover, the above-mentioned binder component has the resistance over the organic electrolytic solution, and the bond strength of the electrode sheet and charge collectors, such as a metal, which use fluorine-containing resin as a binder is also extremely excellent. For this reason, even if it repeats a charge-and-discharge cycle by the high current consistency and impresses an electrical potential difference over a long period of time, the actuation engine performance is stable and the increment in the internal resistance of an electrode can be lessened.

[0020] Since the epoxy resin used for the above-mentioned binder component can come to hand as resin powder or a varnish, it dissolves in a solvent if needed, and considers as a solution, and suspension-like adhesives are obtained by making this solution distribute carbon black and a graphite particle to homogeneity as a conductive filler. Coating of these adhesives is carried out on the surface of a charge collector, and the electrode subsequently to beforehand fabricated in the shape of a sheet to this coating side is carried, it is stuck by pressure, and the electrode object which the electrode and the charge collector unified is acquired by carrying out stoving.

[0021] Since capacity can also make reinforcement high greatly as specific surface area is 700-2500m² / g, especially 1000-2000m² / g, the carbon material of the electrode of the electric double layer capacitor of this invention is desirable. Although activated carbon, carbon black, the poly acene, etc. are mentioned as a carbon material, it is desirable to use especially activated carbon powder, and it is still more desirable when it is used as electric conduction material, adding high conductivity carbon black. In this case, as for electric conduction material, it is desirable to be contained five to 20% of the weight in an electrode.

[0022] Moreover, although a positive electrode and a negative electrode constitute an electric double

layer capacitor using the above-mentioned electrode, either a positive electrode or a negative electrode may be used as the above-mentioned electrode, and the nonpolarizable electrode ingredient in which charge and discharge are possible, i.e., the active material ingredient for rechargeable batteries, may usually be used for another electrode as a principal component.

[0023] It is desirable that fluorine-containing resin is contained in the electrode in this invention as a binder. Since especially polytetrafluoroethylene gives reinforcement to an electrode and cannot check the conductivity of an electrode easily even when it is little by having thermal resistance and chemical resistance and making them fibrous, it is desirable. As for the reinforcement of an electrode, and the viewpoint of conductive balance to a binder, it is desirable to be contained five to 20% of the weight in an electrode.

[0024] The charge collector which connects the above-mentioned electrode electrically is excellent in conductivity, and carbon system ingredients, such as conductive rubber containing noble metals, such as bulb metals, such as aluminum, titanium, and a tantalum, stainless steel, gold, and platinum, a graphite, glassy carbon, or carbon black, etc. can use it preferably that what is necessary is just the ingredient which is electrochemically durable. Since it was lightweight, and it excelled in conductivity and is electrochemically stable especially, aluminum is desirable.

[0025] As for an electrode, it is desirable to be joined to a charge collector through electroconductive glue, after fabricating in the shape of a sheet, and after it kneads the mixture of activated carbon powder, carbon black, fluorine-containing resin, and fluid lubrication material as the production approach of an electrode, for example, it is rolled out, and it is fabricated in the shape of a sheet. Beforehand, the obtained sheet-like electrode carries electroconductive glue on the field which carried out coating, sticks it to a charge collector by pressure, and preferably, under an elevated temperature 150 degrees C or more, by carrying out stoving under reduced pressure still more preferably, electroconductive glue hardens it and it can join an electrode to a charge collector firmly. For the productivity drive of an electrode object, it is still more desirable to carry out reduced pressure drying at 150-170 degrees C.

[0026] Moreover, an electrode makes the solution which dissolved fluorine-containing resin in the solvent distribute a carbon material, may carry out coating of a slurry, and nothing and this slurry to a charge collector, and may form them. It is desirable to carry out coating of the slurry on the field which carried out coating of the electroconductive glue to the charge collector beforehand, and to carry out stoving also in this case, under an elevated temperature 150 degrees C or more, especially reduced pressure.

[0027] Especially the organic electrolytic solution used for the electric double layer capacitor of this invention is not limited, but can use the organic electrolytic solution which contains the salts of ionic dissociation nature in a well-known organic solvent. Especially The 4th class (4 3 2 R1, R R R ***** independently alkyl group of carbon numbers 1-6) onium cation of R1 R2 R3 R4 N+ and R1 R2 R3 R4 P+ etc., It is desirable to use the organic electrolytic solution made to dissolve the salt which consists of anions, such as BF4-, PF6-, ClO4-, and CF3 SO3-, in an organic solvent.

[0028] As the above-mentioned organic solvent, lactone, such as carbonate, such as propylene carbonate, butylene carbonate, and diethyl carbonate, and gamma-butyl lactone, sulfolanes, or these mixed solvents can use it preferably.

[0029]

[Example] The coconut obtained by the steam activation method added and kneaded ethanol into the mixture which consists of 80 % of the weight (10 micrometers of mean diameters, specific surface area of 1800m² / g) of ***** powder, 10 % of the weight of polytetrafluoroethylenes, and 10 % of the weight of carbon black, fabricated the kneading object in the shape of a sheet, carried out roll rolling further at 0.3mm in thickness, and produced the electrode sheet. The electrode sheet of 40mm angle was cut out from this sheet, adhesion immobilization of this was carried out through following electroconductive glue (a) - (h) on the front face of an aluminium foil charge collector with a thickness of 0.1mm which performed etching processing, it heated under reduced pressure for 3 hours at the temperature shown in Table 1, respectively, desiccation processing was carried out, and the moisture in each electrode was removed.

[0030] Move the electrode object joined to the charge collector after desiccation to the glove compartment which filled the argon gas of low humidity, infiltrated enough the propylene carbonate solution which contains the tetraethylammonium tetrafluoroborate of 1 mol/l as the organic electrolytic solution, the electrode of two sheets was made to counter on both sides of the separator paper which consists of a nonwoven fabric of a polypropylene fiber in between, and the electric double layer capacitor was assembled.

[0031] After measuring an early discharge capacity and the internal resistance of an electric double layer capacitor which were obtained, the long-term actuation dependability of an electric double layer capacitor was evaluated accelerative by measuring the discharge capacity and internal resistance after a 3000 cycle repeat and 3000 cycles for the charge and discharge by the constant current of 1A between 0-2.8V in a 40-degree C thermostat, and observing the engine-performance change before and behind a cycle trial. A result is shown in Table 1. In addition, in Table 1, Examples 1-5 are examples of this invention, and Examples 6-8 are examples of a comparison of this invention.

[0032] 10g of [electroconductive glue (a)] conductivity carbon black powder -- the methyl ethyl ketone (80 degrees C of boiling points) was mixed for diethylenetriamine (DETA) as 1.8g and a curing agent, 10g was fully mixed as 0.20g and a solvent, and the bisphenol A type epoxy resin (oil-ized shell epoxy company make, a trade name: Epicoat 827) was prepared.

[0033] It prepared like electroconductive glue (a) except having used 0.23g of triethylenetetramines instead of diethylenetriamine as a [electroconductive glue (b)] curing agent.

[0034] It prepared like electroconductive glue (a) except having used 0.30g of meta-xylylene diamines instead of diethylenetriamine as a [electroconductive glue (c)] curing agent.

[0035] 0.10g was used for the dicyandiamide instead of diethylenetriamine as a [electroconductive glue (d)] curing agent, and methyl-isobutyl-ketone (118 degrees C of boiling points) 2.5g and 2.5g (139 degrees C of boiling points) of meta xylene were prepared like electroconductive glue (a) instead of the methyl ethyl ketone as a solvent except having mixed and used.

[0036] Phenol novolak type Epicoat 154 (oil-ized shell epoxy company make) was prepared like electroconductive glue (a) instead of Epicoat 827 as a [electroconductive glue (e)] epoxy resin except having used 1.8g.

[0037] 2.5g was mixed by making polyimide resin (trade name: U-varnish, Ube Industries, Ltd. make) into solid content, and further, for viscosity control, it diluted with the N-methyl-2-pyrrolidone to 10g of [electroconductive glue (f)] conductivity carbon black powder, and prepared to it.

[0038] 2.5g was mixed by making polyvinyl alcohol system resin (trade name: Gosenol, Japanese synthetic chemistry company make) into solid content, and further, for viscosity control, it diluted with the methyl ethyl ketone to 10g of [electroconductive glue (g)] conductivity carbon black powder, and prepared to it. In addition, since polyvinyl alcohol system resin had low thermal resistance, curing temperature was made into 120 degrees C.

[0039]

[Table 1]

	導電性 接着剤	硬化 温度 (℃)	初期特性		サイクル試験後	
			容量 (F)	内部抵抗 (Ω)	容量 (F)	内部抵抗 (Ω)
例1	(a)	150	15.2	0.52	14.1	0.58
例2	(b)	150	15.5	0.54	14.6	0.60
例3	(c)	150	15.7	0.55	14.8	0.62
例4	(d)	160	15.2	0.56	14.9	0.63
例5	(e)	150	15.0	0.53	14.5	0.64
例6	(f)	150	14.8	0.60	10.0	0.98
例7	(f)	400	15.3	0.52	14.5	0.54
例8	(g)	120	14.4	0.66	8.4	1.32

[0040] [Effect of the Invention] Although the electric double layer capacitor of this invention stiffened electroconductive glue at comparatively low temperature when a charge-and-discharge cycle trial is performed at an elevated temperature and evaluated accelerative, its rise of capacity reduction and internal resistance is small. According to this invention, even if it uses it for a long period of time, there is little performance degradation, and the electric double layer capacitor excellent in actuation dependability can be offered.

[Translation done.]